Chapter 2
History of Stereolithographic Processes

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2.1 Introduction

There are a number of processes that can realize three-dimensional (3D) shapes such as those stored in the memory of a computer. An example is the use of holographic techniques [1], but these require many complex calculations to obtain the hologram and there is insufficient accuracy and clarity. A manual or a conventional mechanical process can also make a physical model, but such models require long fabricating times, high cost and excessive labor. To solve these kinds of problems, a new group of techniques called additive manufacturing (AM) technologies have been developed over the last 10 numbers [2–14].

AM is a collection of processes in which physical objects are quickly created directly from computer generated models. The basic concept of rapid prototyping is where 3D structures are formed by laminating thin layers according to two-dimensional (2D) slice data, obtained from a 3D model created on a CAD/CAM system [2–15].

Stereolithography is one of the most popular AM process. It usually involves the curing or solidification of a liquid photosensitive polymer by a laser beam scanned across its surface. The laser supplies energy that induces a chemical reaction, bonding large number of small molecules and forming a highly cross-linked polymer [16].

2.2 The Importance of a Prototype

In today’s highly competitive marketplace with short life cycles of products, developing a new product to meet consumers’ needs in a shorter lead time is very important for an enterprise. Facing this environment, the strategy of developing a product is transformed from “product-push” type to “market-pull”. Thus, to
improve competitiveness, a product should not only satisfy consumers’ physical requirements, but also should satisfy their needs, increasing the product complexity and reducing its lifetime [16, 17] as shown in Fig. 2.1. Besides, market segmentation has resulted in demand from individualistic consumers, which has led to the concept of “niche markets” increasing product choice [18]. Moreover, companies must meet customer expectations in terms of improved quality and lower cost of products. These new strategies adopted by modern companies lead to a tremendous change in their internal flexibility. As a consequence, the current industrial trend is moving from mass production, i.e. high volume and small range of products for manufacturing, to small volume and a wide range of products [18].

As a consequence of the increasing globalization, companies are now facing competition from low cost and newly industrialized countries putting market prices under pressure [16, 19]. Besides, technology development is increasing rapidly and ecological factors also became important sources of pressure [19]. International markets are therefore highly volatile and competition is brutal, imposing new demands on the innovative ability of companies. Moreover, it becomes increasingly important to rapidly develop new and successful products, requiring changes on how a product is developed. Thus, different groups in a company must cooperate more closely towards a common goal. This must be clear to everyone involved, and if cooperation is to be effective, it is essential to avoid communication problems [3].
According to Krouwel [20], the product development process encompasses five different phases: the information phase, concept phase, engineering phase, tooling phase, and production phase. The information phase encompasses market research, analysis of patents and competing products, etc. The concept phase corresponds to the design-modeling step and is generally the phase where a computer model is created (virtual or soft prototyping phase) [3]. In the engineering phase, engineers study the product in order to find the best and most simple technological solution in order to implement the initial concept. During this phase, a prototype of the product is usually made and tested. Only after the engineering phase is completed the tools, preparation for manufacturing (tooling phase) and the production phase will start. These first three phases represent almost 50% of the product development cycle and among them the engineering phase can represent 25–40% [20]. These phases are performed in a sequence, which means that any serious error detected in the engineering phase implies a new concept phase and repetition of the process. Therefore, for most products the majority of development time occurs in the concept and engineering validation phases, and changes to a design become more costly as they approach the production phase [3, 20]. Moreover, with more complex products, the probability of errors increases dramatically. Thus, it is important to identify any inconsistencies or problems early on. The possibility of creating a computer model of the product to be manufactured, and at the same time using that model to create a prototype, aids in this process by helping to ensure that the product which is going to be produced is exactly the way the product designers, engineers, and customers want it. Through the prototypes, product designers and engineers can get feedback on design information for optimization as well as for further manufacturing processing, reducing errors from incorrect interpretation of the design [3]. Moreover, fabrication of a prototype of the product in the concept phase provides the possibility of starting the engineering phase almost in parallel, reducing significantly the product development cycle. This way, prototypes can be important communication tools as well as useful tools for testing the concept to see if it performs as required or needs improvement, and for esthetic assessment, minimizing time-consuming discussions and evaluations [2, 3].

AM as a group of processes for the rapid production of models also provides the necessary support for the adaptation of simultaneous or concurrent engineering. Simultaneous engineering (SE) is a strategy of bringing all the teams in a company to participate together at an early stage in the design process. SE methodology requires everyone in the company to perform their tasks in parallel, in contrast with traditional manufacturing processes where the product idea moves sequentially through the company (see Fig. 2.2).

AM also enables effective implementation of reverse engineering (RE), permitting the redesign of an existing product. Through RE, the shape of an existing product is digitized, creating the correspondent surface model, which can then be manipulated (re-design process), and finally the model of the new product can be produced using AM processes [22–25].
2.3 Techniques to Produce Prototypes

The traditional way to make a physical model or prototype, besides hand-made wood or clay models, is to use numerically controlled machines as CNC (computer numerical control) milling, electric-discharge machining, turning, and grinding machines [26, 27].

In such processes, the object is revealed by cutting away material from a starting block and therefore these processes are called subtractive methods [3, 26–28]. While conventional machine tools are usually effective in producing the desired object, they are deficient in many respects. First, a large amount of waste material for disposal is produced. Further, such methods usually require expensive object-specific tooling, the setting up of machining protocols, and generation and programming of 3D tool paths which all require much time and a great deal of human judgement and expertise. The cost and time to set up and run machine-specific tooling, along with the initial costs for tooling, make conventional manufacturing processes both time and cost intensive for small productions like models or prototypes [28].

The final difficulty associated with such processes is the impossibility of making special object configurations [3, 26, 27]. Effectively, these conventional methods are usually best suited for producing symmetrical objects and objects where only the exterior is machined. However, when a desired object has an unusual shape or specific internal features, the machining becomes more difficult and quite often the

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**Fig. 2.2** Comparison between the traditional manufacturing system and the new manufacturing approach through AM technologies [21]
object must be divided into segments for production [3, 26, 27]. In many cases, a particular object configuration is not possible because of the limitations imposed upon the tool.

Other important classes of conventional manufacturing processes are the so-called formative methods [3], e.g. casting, injection molding, compressive molding, etc. Through these processes the material is forced into the desired shape using molds, in which the material is made to harden and solidify. However, these processes are still often highly expensive, time consuming, and require a broad range of expertise.

Recently, AM emerged as a step forward in the product cycle, reducing lead times for new products, as well as improving design manufacturing and tooling costs [2–14]. In AM, a single automated system can be used to produce models directly from engineering designs. Such systems are limited only by the size of the model and not by its complexity [2, 3].

AM technologies are additive methods [2–14] because they build objects layer by layer, and as a consequence they are also generally known as Layered Manufacturing Techniques [8, 9]. AM processes are similar processes to 2D printing and plotting technologies using both vector-based and raster-based imaging techniques. The various AM processes include laser sintering, lamination, extrusion, ink-jet printing, and photolithographic systems [2–14, 16]. AM technologies have been mainly used for [2–5, 13, 16, 29–38]:

- Physical verification of a previously defined CAD model
- Form, fit, and function testing
- Creating models without regard to draft angles, parting lines, etc
- Concept presentations and design reviews
- Direct tooling as well as masters for rapid tooling, using conversion technologies such as investment casting and silicone, epoxy and spray metal molds
- Reducing time-to-market
- Creating anatomical models constructed from computer-aided tomography data for surgical planning, prosthesis design, scaffolds for tissue engineering and dental implants
- Producing relief models for geographical applications
- Creating 3D portraits (three-dimensional photography) using data produced by 3D shape digitizing technology.

### 2.4 Stereolithographic Processes

Photolithographic systems build shapes using light to selectively solidify photosensitive resins. There are two basic approaches:

- Laser lithography
- Photo-mask
The laser lithography (or Stereolithography) approach is currently one of the most used AM technologies. Models are defined by scanning a laser beam over a photopolymer surface. Photo-mask systems build models by shining a flood lamp through a mask, which lets light through it and is a method commonly employed in microlithography.

2.4.1 History and Development of the Photolithographic Systems

Lithography is the art of reproduction of graphic objects and comprises different techniques, such as photographic reproduction, photosculpture, xerography and microlithography. Modern photolithographic AM systems harness the principle of computer generated graphics combined with photosensitive materials to produce 3D objects.

Photosensitive materials have been known at least since the time of the ancient Egyptians and probably long before them. The alchemists of the Middle Ages and Renaissance knew about the phenomena of blackening silver salts by light exposure. However, they did not realize that this phenomenon was due solely to the Sun’s light and not to its heat. In fact, they argued that all changes produced in bodies exposed to sunlight were due to heat and not to light [39].

In 1775, Schultz discovered that a silver-containing precipitate used to produce phosphorous, turned purple when illuminated by sunlight, whilst the portion turned away from the light remained white. After that, he divided the mixture into two lots, one of which he kept in the dark, exposing the other to sunlight, with a thin cord tied round the bottle, and again a change in the precipitate exposed to the sunlight was observed. He repeated the experiment by covering the bottle with paper from which he had cut out words and entire sentences, this way “writing” the words and sentences in the solution [39].

Another remarkable achievement was due to Niépce (1822), when he made his first successful and permanent copy of an engraving of Pope Pius VII [39]. He dissolved bitumen of Judea in oil of lavender, and spread a thin layer on a glass plate on which he superimposed an engraving of Pope Pius VII made transparent by oiling. After exposure to light, the bitumen under the white parts of the engraving became hard, whilst that under the dark lines remained soluble [34, 39].

2.4.1.1 Origins of Modern Stereolithography

The first significant work associated with modern photolithographic AM systems only emerged during the 1970s [8, 10]. In 1971, Swainson [40] presented a patent for a system where two intersecting beams of radiation produce a phase change in
a material to build 3D objects. The essential features of this process, named photochemical machining [41], are illustrated in Fig. 2.3. The object through this process can be formed by either photochemically cross-linking or degrading a polymer [42–44]. However, the major problem of this process was due to the photonic absorption by the photopolymeric system used, which occurs somewhere along the paths of each laser, initiating polymerisations in spots that differ from the planned ones [41]. In the 1980s, the idea was abandoned due to funding problems, without achieving optimum working parameters, adequate materials, and good accuracy of final models [34].

Kodama [45] described an automatic method for fabricating 3D models in layered stepped stages using a photosensitive polymer. Light capable of curing the polymer was directed onto the surface, and the desired shape of a layer was created by using an appropriate mask (Fig. 2.4a, b) or an optical fiber manipulated by an X–Y plotter (Fig. 2.4c).

Herbert [46] described the design of two sets of apparatus for producing replicas of solid objects, in a layer-by-layer way, using a photosensitive polymer. The purpose of the first one (Fig. 2.5) was only for the construction of solids of revolution, made by rotating a layer of polymer and focusing a spot of light on the layer. The second apparatus constructed solid objects of any desired cross-section (Fig. 2.6).

Hull conceived the idea of modern stereolithography [47–49]. According to the principles of stereolithography (Fig. 2.7), a 3D object is formed layer by layer in a stepwise fashion out of a material capable of solidification upon exposure to ultraviolet (UV) radiation [47–49]. Moreover, the non-transformed layers typically adhere to the previously formed layers through the natural adhesive properties of the photosensitive polymer upon solidification. Almost in parallel, André, who prepared different patent applications [50, 51] conducted similar work in France.
Fig. 2.4  Schematics of the three systems studied by Kodama [45]

Fig. 2.5  Herbert’s apparatus for construction of solids of revolution [46]
The entire process of conceiving a model using stereolitography (the different phases of the building process are shown in Fig. 2.8) comprises the following steps [2, 3, 16, 47–49]:

1. Create a solid or surface model on a CAD system
2. Export the CAD model
3. Add support structures
4. Specify the build style variables and parameters necessary for slicing
5. Slice the computer model to generate the information that controls the SL apparatus

Fig. 2.6 Herbert’s apparatus for generating models by polymerisation [46]

Fig. 2.7 Hull’s stereolithography process [47]
6. Build the model using the slice file
7. Post-process and clean the part
8. Post-curing to complete the cure process.

The block diagram of the stereolithography system as proposed by Hull [47, 48] is shown in Fig. 2.9.

Fig. 2.8 Flowchart of the stereolithography building process [47]
Hull also proposed other stereolithographic strategies as shown in Fig. 2.10. In this system the physical object is pulled up from the liquid resin, rather than down and further into the liquid photopolymeric system [47]. The radiation passes through a UV transparent window.

In order to minimize the amount photopolymerisable material required for the fabrication process, Murphy et al. [52] proposed a stereolithographic method and apparatus in which a membrane separates two liquid phases. The system (Fig. 2.11)
comprises a nonpolymerisable fluid phase, an impermeable movable membrane positioned on top of the fluid phase, a photopolymerisable liquid resin positioned on top of the membrane and a radiation source positioned above the polymerisable material [52].
Almquist and Smalley [53] proposed the concept of thermal stereolithography that uses a solid material, instead of a liquid one, which is flowable when subjected to light.

Marutani [54, 55] has proposed a new stereolithographic system that polymerises a liquid resin inside the vat rather than at the surface. In this system a UV laser beam penetrates through a pipe into the vat containing the liquid resin and solidifies it, thereby eliminating the need for successive layer deposition as in conventional stereolithography.

An important evolution step in the stereolithography domain is the so-called color stereolithography [56]. This process uses a clear liquid resin containing additives that color upon exposure to high doses of UV radiation. Through this process, each layer is cured in the usual way, using a dose of UV radiation sufficient for curing but not for coloring. When the “writing” process of each layer is completed, the laser rescans the area required to be colored at a lower speed, delivering in this way a much higher dose of UV radiation. This provides a means to highlight features in a model and, since the uncolored stereolithography resins are transparent, to show features that may be embedded inside the encompassing solid object. A more laborious coloring strategy was proposed by Im et al. [57] (Fig. 2.12).

![Fig. 2.12](image-url)  
**Fig. 2.12** Colouring stereolithography [57]
In order to eliminate the need of support structures, Murakami [58, 59] proposed a stereolithographic approach for fabricating solid (cured) objects from solid (non-cured) photopolymeric resin (Fig. 2.13). First, a liquid resin is supplied to form a new layer, cooled to the gel state (between $-50$ and $-10^\circ$C), and then selectively photopolymerised. The final object is revealed by heating the gel resin block [58–60].

Other important inventions are listed on Table 2.1.

### 2.4.1.2 Photomask Systems

Pomerantz [61, 62] proposed a photomask system to produce 3D models (Fig. 2.14). The steps of his technique, currently known as Solid Ground Curing (SGC), are: deposit a thin layer of polymer; illuminate the polymer through a xerographically produced mask having geometry of a single cross section; removal by suction of the uncured material; fill the areas vacated by the uncured material with water or wax; cure or freeze the rest of the layer; grind the surface to establish a uniform layer; repeat the earlier steps until the model is complete.

Fudim [63, 64] developed a technique similar to the Pomerantz method. His technique [63, 64] involves the illumination of a photosensitive polymer, with UV radiation through masks and a piece of flat material transparent to the radiation that remains in contact with the liquid layer being formed. The method is simpler than the SGC technique, but requires an operator to create and manually position each mask.

Photomasking systems generally require the generation of many masks, and precise mask alignments. One solution to this problem is to use a liquid crystal...
### Table 2.1 Other relevant laser lithography patents

<table>
<thead>
<tr>
<th>Inventors</th>
<th>Topic</th>
<th>Patent</th>
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<tbody>
<tr>
<td>Hull et al.</td>
<td>Discloses various removable support structures for stereolithography</td>
<td>US Patent 4999143</td>
</tr>
<tr>
<td>Modrek et al.</td>
<td>Presents techniques for post processing objects produced by stereolithography</td>
<td>US Patent 5076974</td>
</tr>
<tr>
<td>Spence et al.</td>
<td>Proposes the use of multiple wavelengths in the exposure of a stereolithographic medium</td>
<td>US Patent 5182056</td>
</tr>
<tr>
<td>Hull et al.</td>
<td>Discloses a program called Slice and various techniques for converting 3D object data into data descriptive of cross-sections</td>
<td>US Patent 5184307</td>
</tr>
<tr>
<td>Allison et al.</td>
<td>Proposes various build/exposure styles and various techniques for reducing object distortion</td>
<td>US Patent 5256340</td>
</tr>
<tr>
<td>Almquist et al.</td>
<td>Proposes various recoating techniques for stereolithography. Presents techniques such as (1) an inkjet dispensing device, (2) a fling recoater, (3) a vacuum applicator, (4) a stream recoater, (5) a counter-rotating roller recoater, and (6) a technique for deriving sweep extents</td>
<td>US Patent 08/790005</td>
</tr>
<tr>
<td>Partanen et al.</td>
<td>Proposes the application of solid-state lasers to stereolithography</td>
<td>US Patent 08/792347</td>
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<tr>
<td>Partanen et al.</td>
<td>Discloses the use of a pulsed radiation source in stereolithography</td>
<td>US Patent 08/847855</td>
</tr>
<tr>
<td>Bloomstein et al.</td>
<td>Presents a stereolithographic patterning system with variable size exposure areas</td>
<td>US Patent 633234</td>
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**Fig. 2.14** The photo-fabrication system proposed by Pomerantz [61]
display (LCD) or a digital processing projection system as a reconfigurable mask [16]. Through this process, the CAD model is converted to a grayscale contour map, and the LCD mask modulates the light intensity distribution according to the gray-scale contour map of the model. However, due to the large pixel size and very low transmission in UV, the device’s resolution is limited and contrast is poor. Therefore, several stereolithographic systems using a Digital Micromirror Device as a dynamic mask have been proposed (Fig. 2.15) [65, 66].

Recently Murakami [60] from the University of Tokyo, Japan, proposed a new stereolithographic system involving the separate use of a liquid photo-initiator and a photopolymer without photoinitiator. In this process (Fig. 2.16), the resin without photoinitiator is supplied as a layer, and then a mask pattern is drawn onto the surface with photoinitiator by inkjet printing. When the surface is exposed to UV light, only the pattern drawn with the photoinitiator, which acts as a positive mask, is cured.
Fig. 2.16 Stereolithography process using positive direct-mask exposure [60]

References


